

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**



POLYGLOT LANGUAGE SERVICE

Translations for Industry Worldwide

340 Brannan Street, Suite 305
San Francisco, CA 94107 • USA

Tel (415) 512-8800

Fax (415) 512-8982

TRANSLATION FROM JAPANESE

- (19) JAPANESE PATENT OFFICE (JP)
(12) Official Gazette for Laid-Open Patent Applications (A)
(11) Japanese Laid-Open Patent Application (Kokai) No. 4-352771
(43) Laying-Open Date: December 7, 1992

(51)	Int. CL ⁵ :	Classification Symbols:	Internal Office Registration Nos.:	FI
	C 07 D	301/06	7822-4C	
	B 01 J	21/16	X 8017-4G	
		29/04	X 6750-4G	
	C 07 D	303/04	7822-4C	
	//C 07 B	61/00		
		300		

Request for Examination: Not yet submitted
(Total of 5 pages [in original])

Number of Claims: 1

- (21) Application No.: 3-150850
(22) Filing Date: May 28, 1991
(71) Applicant: 000003300

Tosoh Corp.

- (72) Inventor: Akira Sato
(72) Inventor: Takanori Miyake

- (54) [Title of the Invention] A Method for Manufacturing Propylene Oxide
(57) [Summary]

[Objective]

To offer an economical method for highly selective manufacture of propylene oxide without co-products.

[Structure]

Propylene oxide is obtained from a reaction of propylene, hydrogen, and oxygen, using a catalyst comprising a Group VIII metal from the periodic table and a crystalline titanosilicate.

[Claims]**[Claim 1]**

A method for manufacturing propylene oxide, which is characterized by the fact that a reaction of propylene, hydrogen, and oxygen is brought about using a catalyst comprising a Group VIII metal from the periodic table and a crystalline titanosilicate.

[Detailed Description of the Invention]**[0001]****[Field of Industrial Utilization]**

The present invention concerns a method for manufacturing propylene oxide, which serves an important role industrially as a starting material for polypropylene glycol and the like.

[0002]**[Prior Art]**

Known methods for manufacturing propylene oxide include the chlorohydrin process, wherein calcium chloride is produced as a byproduct, the Halcon process, wherein t-butyl alcohol and styrene monomers are co-produced, and a peracetic acid process, in which acetic acid is co-produced.

[0003]

A method wherein a hydroperoxide is used as an additional starting material and a crystalline titanosilicate is used as a catalyst is also known (see, for example, US Patent 4,833,260).

[0004]**[Problems Which the Invention Is Intended to Solve]**

However, in the above-mentioned chlorohydrin process, the chlorine was utilized inefficiently since dehydrochlorination with a lime emulsion was subsequently performed, and the large amounts of calcium chloride produced as a by-product required treatment. In the Halcon and peracetic acid processes, an assured market for the large amounts of coproducts was required, and processes involving the use of hydroperoxides required equimolar or greater amounts of high-cost hydroperoxides, posing problems of economy.

[0005]

It was therefore desirable to develop a highly selective method for manufacturing epoxy compounds, which would not produce co-products and would not entail the use of high-cost hydroperoxides as starting materials.

[0006]

[Means Used to Solve the Above-Mentioned Problems]

As a result of painstaking research concerning the above, the inventors discovered that by bringing about a reaction of propylene, hydrogen, and oxygen using a catalyst comprising a Group VIII metal from the periodic table and a crystalline titanosilicate, propylene oxide could be obtained with high selectivity, and thus arrived at the present invention.

[0007]

Specifically, the present invention offers a method for manufacturing propylene oxide, which is characterized by the fact that a reaction of propylene, hydrogen, and oxygen is brought about using a catalyst comprising a Group VIII metal from the periodic table and a crystalline titanosilicate.

[0008]

The method which pertains to the present invention will be described in further detail below.

[0009]

In the method which pertains to the present invention, a catalyst comprising a Group VIII metal from the periodic table and a crystalline titanosilicate is used. The titanosilicate referred to here is obtained by substitution of a portion of the silicon which forms the crystal lattice of "Silicalite" (crystalline SiO_2 having a zeolite structure, developed by E. M. Flanigen (Nature, 271, 512 (1978)) mainly with titanium. The titanosilicate may be synthesized by any desired method; an example of synthesis is disclosed in Japanese Laid-Open Patent Application 56-96720. The amount of titanium contained in said titanosilicate may be defined as the silica/titania ratio (molar), and said silica/titania ratio should be a value of 5 to 200. If the titanium content is too low the activity of the catalyst will be insufficient; conversely, if it is too high the titanosilicate crystal structure will rupture. Components of the titanosilicate are not restricted to titanium: one or more additional elements such as boron.

aluminum, phosphorus, vanadium, chromium, manganese, iron, gallium, or zirconium may also be contained therein without ill effect.

[0010]

The prepared titanosilicate may be used without modification, or molded. It is common to use a binder when preparing a molded form; there are no restrictions regarding the type of binder, which may be silica, alumina, or the like.

[0011]

In the method which pertains to the present invention, a catalyst comprising a Group VIII metal from the periodic table and a crystalline titanosilicate is used, and any of the Group VIII metals may be used as the above-mentioned Group VIII metal. Typical examples include palladium, platinum, iridium, rhodium, ruthenium, and the like; palladium is particularly desirable. The Group VIII metal may be supported on the crystalline titanosilicate, or first supported on silica, alumina, activated carbon or the like and then physically mixed with the titanosilicate. There are no particular restrictions regarding the starting material to be supported when supporting a Group VIII metal; examples include palladium(II) chloride, tetraamminepalladium(II) chloride, and palladium(II) acetate when palladium is used. There are no restrictions regarding the method for supporting these metals on the titanosilicate: an immersion method or the like may be used.

[0012]

The periodic table Group VIII metal content, with respect to the titanosilicate, should be 0.1 to 10 wt% as metal atoms. Efficacy will be diminished if the content falls below 0.1 wt%, and amounts in excess of 10 wt% are undesirable from an economic standpoint. When the periodic table Group VIII metal is supported on titanosilicate using an immersion process, the catalyst may be baked and/or reduced prior to use. Baking may be performed under a stream of an inert gas or an oxygen-containing gas. There are no particular restrictions regarding baking temperature and duration, but baking at 100 to 700°C for 30 minutes to 24 hours is satisfactory. When reduction is performed, there are no particular restrictions regarding the reducing agent or the reduction temperature and duration as long as the metal component is reduced; reduction at room temperature to 500°C for 30 minutes to 24 hours using hydrogen as a reducing agent is satisfactory.

[0013]

The prepared catalyst may be used without modification or by adding a diluent such as silica or alumina prior to use in reactions. The prepared Group VIII metal-supporting zeolite catalyst may be reduced under a hydrogen-containing gas flow prior to use in reactions.

[0014]

If necessary, a solvent may be used when bringing about a reaction. Polar solvents such as water, alcohols having a carbon number of 6 or less, ketones, glycols, and carboxylic acids may be used as solvents.

[0015]

The reaction process may be of a continuous flow, semi-batch, or batch type; a continuous flow process is preferable from a productivity standpoint.

[0016]

The reaction temperature should be 0 to 150°C, and preferably 10 to 100°C. If a solvent is to be used and the reaction temperature exceeds the boiling point of said solvent, the reaction may be brought about after pressurization. There are no particular restrictions regarding the reaction pressure, but it is ordinarily within the range of normal pressure to 200 atmospheres.

[0017]

In the method which pertains to the present invention oxygen is used as one of the starting materials for the reaction. It is possible to use an oxygen-containing gas such as air.

[0018]

There are no particular restrictions regarding the amounts of the several starting materials contained in the gas. [A mixture of] 10 to 50 vol% propylene (C_3H_6), 5 to 40 vol% hydrogen (H_2), and 5 to 50 vol% oxygen (O_2), for example, is possible. From the standpoint of safety, it is desirable for the contained amounts of the several starting materials to be outside of the explosive range. [The gas] may be diluted with an inert gas such as hydrogen.

?

[0019]

The amount of the catalyst used in the reaction may be determined on the basis of the ratio (molar) of the titanium within the titanasilicate to one of the starting materials, propylene, that is supplied per unit of time; it is desirable to use an amount of the catalyst such that the titanium/propylene ratio is 0.00001 to 0.1. *fine?*

[0020]

The time required for the reaction may be determined on the basis of the gas [hourly] space velocity (the total volume of the C_3H_6 , H_2 , O_2 , and inert gas per hour/unit of catalyst volume; hereinafter abbreviated as GHSV). A GHSV of 2000 to 40,000 hr^{-1} ($20^\circ C$) is satisfactory.

[0021]

[Merits of the Invention]

In the present invention, it is possible to obtain propylene oxide with high selectivity, without coproducts, and without the use of high-cost hydroperoxides by means of bringing about a reaction of propylene, hydrogen, and oxygen using a catalyst comprising a Group VIII metal from the periodic table and a crystalline titanasilicate, and the invention is therefore highly significant to industry.

[0022]

[Practical Examples]

The present invention will be described in further detail below through practical examples; however, these are intended merely to describe the present invention, which is not limited to these practical examples.

Practical Example 1

A titanasilicate having a silica/titania ratio of 67 (as determined by ICP spectrometry) was prepared according to the method in Japanese Laid-Open Patent Application 56-96720, and a tetraamminepalladium(II) chloride solution added until the weight of the palladium atoms reached 0.5 wt% with respect to the titanasilicate. The mixture was mixed by stirring for one hour, evaporated to dryness, and reduced at $150^\circ C$ under a dilute 5% hydrogen gas flow for one hour to yield a catalyst.

[0023]

A normal pressure, liquid phase, continuous flow reaction device was used for the reaction.

[0024]

Δ , H_2 , O_2
24, 16, 16 ml/min at 20°C
1.0 g of the catalyst was suspended in 60 mL 1-butyl alcohol, and C_3H_8 , H_2 , and O_2 supplied thereto at 60, 40, and 40 mmol/hr respectively, and diluted with nitrogen so that GHSV was 7970 hr⁻¹ (20°C). The reaction temperature was 45°C.
if cat. $\rho = 1 \rightarrow 60\% N_2$ (total = 133 ml/min)
" " " = 0.5 $\rightarrow 80\% N_2$ " : 266 "

[0025]

The reaction product was analyzed by gas chromatography. Results over a period from initiation of the reaction to 5 hours thereafter are shown in Figure 1. Selectivity of the products at the fifth hour after initiation of the reaction was 98.6% for propylene oxide and 1.4% for propane (C_3H_8).

0.56% A Conv.
0.019 g PO/g cat-hr

[0026]

Practical Examples 2 and 3

Reactions were brought about by the same procedure as in Practical Example 1, with the exception that C_3H_8 , H_2 , and O_2 were supplied in amounts of 60, 80, and 40 mmol/hr and 60, 40 and 80 mmol/hr respectively. Results five hours after initiation of the reactions are shown in Table 1.

[0027]

[Table 1]

	Starting Material Feed (mmol/hr)			PO ^{a)} (mmol)	Selectivity (%)	
	C_3H_8	H_2	O_2		PO ^{a)}	C_3H_8
Practical Example 2	60	80	40	0.67	92.0	8.0
Practical Example 3	60	40	80	1.83	99.1	0.9

^{a)} Propylene oxide

Practical Examples 4 and 5

Reactions were brought about by the same procedure as in Practical Example 1, with the exception that catalysts in which the weight of the palladium atoms (Pd) with respect to the titanosilicate were 2 and 5 wt% respectively were used. Results five hours after initiation of the reactions are shown in Table 2.

[0028]

[Table 2]

	Supported Pd (%)	PO ^{a)} (mmol)	Selectivity (%)	
			PO ^{a)}	C ₃ H ₈
Practical Example 4	2	0.45	99.1	0.9
Practical Example 5	5	0.37	>99.9	tr.

^{a)} Propylene oxide

Practical Examples 6 through 9

Reactions were brought about by the same procedure as in Practical Example 1, with the exception that a titanosilicate having a silica/titania ratio of 33 was used as the titanosilicate supporting the palladium, and the reaction temperatures were set at 25, 45, 65, and 82°C respectively. Results five hours after initiation of the reactions are shown in Table 3.

[0029]

[Table 3]

	Reaction Temperature (°C)	PO ^{a)} (mmol)	Selectivity (%)	
			PO ^{a)}	C ₃ H ₈
Practical Example 6	25	1.51	98.8	1.2
Practical Example 7	45	2.16	98.8	1.2
Practical Example 8	65	1.37	98.1	1.9
Practical Example 9	82	1.06	98.3	1.7

A conv. = 0.73 %
0.025 g PO/g cat-h.

^{a)} Propylene oxide

Practical Example 10

A reaction was brought about by the same procedure as in Practical Example 1, with the exception that a titanasilicate having a silica/titania ratio of 33 was used as the titanasilicate supporting the palladium, and water was used as a reaction solvent. Five hours after initiation of the reaction, 1.56 mmol propylene oxide was obtained. Selectivity of the products at the fifth hour after initiation of the reaction was 99.8% for propylene oxide and 0.2% for propane.

[0030]

Practical Examples 11 and 12

Reactions were brought about by the same procedure as in Practical Example 1, with the exception that catalysts in which titanasilicate having a silica/titania ratio of 15 supporting the metals palladium and platinum (supported % = 0.5 wt%), respectively, were used. Results five hours after initiation of the reactions are shown in Table 4.

[0031]

[Table 4]

	Supported Metal	PO ^{a)} (mmol)	Selectivity (%)	
			PO ^{a)}	C ₃ H ₈
Practical Example 11	Pd	3.72	99.8	0.2
Practical Example 12	Pt	1.25	98.8	1.2

^{a)} Propylene oxide

$\text{conv. A} = 1.24$
 $\frac{0.0439 \text{ Pt}}{9 \text{ cat.}}$
 $\frac{1.34161}{4^{\text{th}} - \text{hr}}$
 \downarrow
 cat. if p=

Practical Example 13

A reaction was brought about by the same procedure as in Practical Example 1, with the exception that a pulverized mixture of 1 g of a 0.5 wt% palladium-supporting activated carbon catalyst (manufactured by Nihon Engelhard) reduced with hydrogen for one hour at 150°C and 1 g of a titanasilicate having a silica/titania ratio of 33 was used as the catalyst. Five hours after initiation of the reaction, 1.36 mmol propylene oxide was obtained. Selectivity of the products at the fifth hour after initiation of the reaction was 99.8% for propylene oxide and 0.2% for propane.

[Brief Description of the Figures]

[Figure 1]

Figure 1 shows a graph describing the relationship between elapsed time and propylene oxide production in the propylene epoxidation process of Practical Example 1.

[Figure 1]

